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A versatile polar-embedded polyphenyl phase for multimodal separation in liquid chromatography

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ABSTRACT

A new polar-embedded aromatic stationary phase has been prepared by covalently attaching *p*-biphenylacetamide silane to silica spheres. The retention behavior of this phase was compared with an alkylamide counterpart and octadecyl phases using different classes of analytes, including geometric isomers and congeners from Standard Reference Materials 869b, 870 and 1647e, positional isomers of electron-deficient benzenes, as well as alkylbenzenes and alkylbiphenyls. The relationship between shape selectivity and surface chemistry of stationary phase was comparatively studied. Influences of the embedded group and ligand length and/or size on the chromatographic selectivity towards various congeners were established. The new polar-embedded aromatic phase possessed unique benzenoid affinity, enhanced aromatic selectivity, distinct charge-transfer properties, as well as good water-wettability, as a result it can be employed in normal phase, reversed-phase and *per*-aqueous modes.

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1. Introduction

Silica gel with chemically bonded octyl (C8), octadecyl (C18) and triacontyl (C30) phases is imperative in reversed-phase high-performance liquid chromatography (RP-HPLC) [1]. Novel chromatographic adsorbents have been increasingly introduced by incorporating polar species into the stationary phases. These polar species include ether [2], (sulfon-) amide [3–7], (thio-)urea [8–11], carbamate [12–16], phosphate [17], ammonium [18] and imidazolium cations [19]. The range of polar groups studied is wide, partly on account of the plentiful alkyl derivatives and reliable synthetic techniques. The immediate benefits of such structural modification are enhanced retention of polar solutes and enhanced tolerance to highly aqueous mobile phase, even pure water, in which conventional C8 and C18 phases tend to be “de-wetted” and lose retention [20–22]. Generally, the hydrophobic character of the bonded phase is lowered by the embedded polar groups,

whereas various retention mechanisms, e.g. hydrogen-bonding, electrostatic attraction/impulsion, π - π stacking and steric discrimination are possible. Apart from alkyl stationary phases, there is another class of stationary phases providing complementary selectivity, i.e. aromatic stationary phases [23]. In contrast to alkyl stationary phases, types of aromatic stationary phases are limited. Commercial examples include phenyl, diphenylmethane and pyrene. Polar-embedded aromatic stationary phases have been studied that include, besides benzene [24], derivatives of naphthalene [25], anthracene [26–28] and pyrene [29], all of which are condensed-ring polycyclic aromatic hydrocarbons (PAHs).

Polar-embedded alkyl phases are noted for their unique characteristics, such as improved retention of and enhanced selectivity towards polar compounds, as unveiled by the in-depth and systematic studies in the past years [30]. More noticeably, the incorporated polar groups, such as amide, carbamate and imidazolium cation, were frequently found to enhance the selectivity towards compounds with multiple conjugated unsaturated bonds, for instance geometric isomers of PAHs [31,32] and *cis/trans*-isomers of carotenoids [6]. This behavior was believed to be influenced by π - π interactions with the inset polar groups. This shape-related differentiation ability was named “shape selectivity” [33,34], which enabled the resolution of isomeric PAHs by not only hydrophobicity, but also molecule shape and density of π elec-

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trons. On C18 and polar-embedded C18 phases, the elution order of isomeric PAHs follows that of their molecular length/breadth ratio (L/B ratio) [35,36], viz. the retention of solute with larger L/B ratio (e.g. tetracene, more rod-like) is stronger than solute with smaller L/B ratio (e.g. triphenylene, more plate-like). This selectivity was impacted by several factors, including intrinsic properties of ligand length [37], ligand density and functionalization [38], and extrinsic properties of column temperature, mobile phase composition and concentration [39].

Currently it is still unclear whether the enhanced shape selectivity of polar-embedded C18 phase originates solely from the polar group or was a consequence of the combination of the polar group and the increased phase length that resulted from the polar species in the functionalized ligand, even controversially it was found that shape selectivity could be independent of the embedded polar group [40]. According to the literature [41], longer ligands (C30) exhibited higher shape selectivity than shorter ligand (C18) at the same bonding density. In the absence of differences in chain conformation, polar-embedded C18 phases should be longer than regular C18 phases, due to the use of various γ -functional alkylalkoxysilane linkage, for example γ -aminopropyltriethoxysilane and γ -isocyanatopropyltriethoxysilane. Shape selectivity is known to change as a function of bonding density, because bonding densities vary notably from each other in published studies, the reliability from selectivity comparison needs improving.

In this work, we proposed an amide-embedded biphenyl stationary phase. In an effort to determine the influence of embedded polar group on the chromatographic behaviors, this new phase was comparatively studied with an amide-embedded alkyl stationary phase and two C18 stationary phases, focusing on shape and planar selectivity. Due to the rich π electrons of biphenyl, the new phase's charge-transfer behavior towards π electron-deficient solutes was investigated in RP mode. Finally, the multimodal separations using the new phase were demonstrated in different LC modes.

2. Experimental

2.1. Reagents and materials

Ultrapure spherical porous silica (diameter: 5 μm , pore size: 100 \AA , surface area: 350 $\text{m}^2 \text{g}^{-1}$) and monomeric Fuji C18 silica (diameter: 5 μm , pore size: 100 \AA , surface area: 350 $\text{m}^2 \text{g}^{-1}$, carbon content 18%) from Fuji Silysia Chemical Ltd. (Aichi, Japan) were used. *p*-Biphenylacetic acid (99%), tetradecanoyl chloride (99%), *p*-alkylbiphenyls, sulfonamides and nucleosides were purchased from Sun Chemical Technology Co. Ltd. (Shanghai, China). Formic acid (99%), 3-aminopropyltriethoxysilane (APTES, 99%), thionyl chloride (SOCl_2 , 99%) and triethylamine (Et_3N , 99%) were purchased from Aladdin Industrial Corporation (Shanghai, China). Standard Reference Material (SRM) 869b, column selectivity test mixture for liquid chromatography, and SRM 1647e, priority pollutant PAHs, were obtained from the Standard Reference Materials Program (NIST, Gaithersburg, MD, USA). Another column test mixture with composition same to SRM 870 was prepared in acetonitrile (MeCN) by individual solute of highest purity. Trimethylchlorosilane (TMCS), single PAH solute, alkylbenzenes and other solutes were supplied by J&K Chemical (Beijing, China). Ultrapure water (18.3 $\text{M}\Omega$ at 25 $^\circ\text{C}$) was produced by a Milipore Direct Q 3UV unit; methanol (MeOH), ethanol (EtOH), MeCN, *iso*-propanol (IPA), *n*-hexane and tetrahydrofuran (THF) of HPLC grade were used. Solvents for syntheses were dried and distilled prior to use. To better understand the differences in shape selectivity, a homemade polymeric C18 silica phase (C18_p) was included. Applying the method proposed by Sander and Wise [42], this polymeric C18 prepared using octadecyltrichlorosilane had a bonding density

much higher than that of the other three. This polymeric phase was only used for the selectivity study on PAHs.

2.2. Preparation of polar-embedded biphenyl and C14 stationary phases

Following the procedure in previous work [7], the adsorbents were synthesized as below:

(1) Monomeric polar-embedded biphenyl adsorbent: *p*-biphenylacetic acid (1.560 g, 7.35 mmol, 1.05 equiv.) was converted to acyl chloride by excessive SOCl_2 in toluene at 80 $^\circ\text{C}$. Afterwards solvent and residual SOCl_2 were distilled off, leaving a grey solid, which was re-dissolved in 15 mL of toluene and added dropwise to a solution of APTES (1.550, 7 mmol, 1.00 equiv.) and Et_3N (0.850 g, 8.4 mmol, 1.20 equiv.) in 20 mL of toluene in 30 min at ambient temperature. Shortly upon the completion of addition, hydrochloride of Et_3N appeared as white precipitation. The mixture was stirred for another 2 h then heated at 80 $^\circ\text{C}$ for 3 h. The mixture was cooled to room temperature and filtered to remove salt, the filtration was good enough for bonding. The new silane N-triethoxysilylpropyl 4-biphenylacetamide could be isolated via evaporation of toluene and subsequent recrystallization from cyclohexane as a sticky powder with yellowish color (yields > 95%), pure enough for NMR characterizations. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) 6.90–7.40 (9H, m, benzene H), 3.83 (6H, m, $(\text{CH}_3\text{-CH}_2\text{O})_3$), 3.40 (2H, s, benzyl H) 3.17 (2H, m, $\text{CH}_2\text{-NH}$), 1.61 (2H, t, $\text{Si-CH}_2\text{-CH}_2$), 1.37–1.14 (9H, t, $(\text{CH}_3\text{-CH}_2\text{O})_3$), 0.67–0.58 (2H, t, Si-CH_2).

The modification of silica was performed as follows: 5 g of silica gel was dried in vacuum at 140 $^\circ\text{C}$, and suspended in 15 mL of toluene, which was added to the foregoing filtrate under mechanic stirring. The suspension was refluxed for 24 h. Finally, the solid was filtered and thoroughly washed by boiling toluene and THF, then hot THF/water (v/v = 2/1) and EtOH (100 mL for each). To lower the residual silanol activity, the obtained silica gel was endcapped by TMCS in toluene. Again, the silica was collected by filtration and washed thoroughly by hot THF and MeOH (150 mL for each). The final silica material, Amide- π^2 , was dried in vacuum at 60 $^\circ\text{C}$ overnight and stored in a brown vial before further usage and characterization.

(2) Monomeric polar-embedded tetradecyl adsorbent: tetradecanoyl chloride (1.814 g, 7.35 mmol, 1.05 equiv.) was dissolved in 15 mL of toluene and added dropwise to a solution of APTES (1.550 g, 7 mmol, 1.00 equiv.) and Et_3N (0.850 g, 8.4 mmol, 1.20 equiv.) in 20 mL of toluene in 30 min at ambient temperature. The mixture was stirred for another 2 h then heated at 80 $^\circ\text{C}$ for 3 h. The mixture was cooled to room temperature and filtered, the filtration was used directly without isolation of the silane intermediate. Immobilization of the silane intermediate was carried out similar to that of Amide- π^2 . The obtained silica gel was also endcapped by TMCS. The final silica material was named Amide-C14. The whole preparation procedure was depicted in Fig. 1.

2.3. Apparatus

The ^1H NMR spectrum were recorded on a Varian INOVA-400 M instrument (Varian, USA) at 400 MHz using tetramethylsilane as reference. The carbon, hydrogen and nitrogen contents of the silica materials were determined by elemental analysis using a Vario EL III element analyzer (Hanau, Germany). Hydrophobicity (octanol-water partition coefficient, $\log P$) values were obtained from EPI Suite (US Environmental Protection Agency), melting points were obtained by simulative calculation using Jean-Claude ONS Melting Point Model 010.

Each of the adsorbents (2.1 g) was suspended in tetrachloromethane (50 mL) and slurry-packed into stainless steel column (150 mm \times 4.6 mm I.D.) using MeOH as propellant solvent

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